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**WO 01/49706 A2**

(54) Title: METHOD TO DECREASE CORROSIVENESS OF REACTANTS IN POLY(ARLENE SULFIDE) POLYMER PRO-  
DUCTION

(57) Abstract: A process is provided for producing a poly(arlene sulfide) polymer in which polymerization reactants comprising an aqueous alkali metal hydroxide and a polar organic compound are pre-reacted at a first temperature to form a mixture, then the mixture is reacted with a sulfur source at a second temperature under conditions sufficient to remove at least a portion of the water that is contained in the mixture, thereafter the thus dehydrated mixture is contacted with at least one dihaloaromatic compound under polymerization conditions.

**METHOD TO DECREASE CORROSIVENESS OF REACTANTS  
IN POLY(ARLENE SULFIDE) POLYMER PRODUCTION**

**FIELD OF THE INVENTION**

This invention relates to poly(Arlene sulfide), (PAS) polymers. In one aspect this invention relates to a process for the preparation of poly(arlene sulfide) polymers wherein a portion of the polymerization reactants are pre-reacted in a two step process prior to being contacted with remaining polymerization reactants under polymerization conditions.

In one embodiment of this invention, polymerization reactants comprising an aqueous alkali metal hydroxide and a polar organic compound are pre-reacted at a first temperature to form a mixture, then the mixture is reacted with a sulfur source at a second temperature under conditions sufficient to remove at least a portion of the water that is contained in the mixture, thereafter the thus dehydrated mixture is contacted with at least one dihaloaromatic compound under polymerization conditions.

**BACKGROUND OF THE INVENTION**

Poly(arlene sulfide) polymers are generally known in the art and have been found useful due to their high chemical and thermal resistance. Processes for the preparation of such poly(arlene sulfide) polymers have been disclosed in the art. In a typical preparation, at least one dihaloaromatic compound, a sulfur source, and a polar organic compound are contacted under polymerization conditions. Often a hydrous sulfur source is selected, or the reaction of the sulfur source with the polar organic compound generates water or liberates water of hydration. Such water can be detrimental to the formation of high molecular weight polymer, and thus it is often removed by dehydrating a pre-polymerization mixture of the sulfur source and polar organic compound. Such processes are typically conducted at relatively high temperatures under pressure in order to maximize the amount of water removed. This process has disadvantages in that the mixture of the sulfur source and polar organic compound is very corrosive and the dehydration vessel must be replaced or repaired more frequently than would be desirable, or the dehydration vessel must be made of expensive materials of construction that are less susceptible to corrosion. It would be

economically desirable to have a process whereby the aqueous mixture of the sulfur source and polar organic compound to be dehydrated could be rendered less corrosive.

#### OBJECTS OF THE INVENTION

It is desirable to provide a process for preparing a poly(arnlene sulfide) polymer in which the dehydration of the aqueous sulfur source is conducted in a two-step process to render the dehydration mixture less corrosive.

#### SUMMARY OF THE INVENTION

In accordance with this invention, polymerization reactants comprising an aqueous alkali metal hydroxide and a polar organic compound are pre-reacted at a first temperature to form a mixture, then the mixture is reacted with a sulfur source at a second temperature under conditions sufficient to remove at least a portion of the water that is contained in the mixture, thereafter the thus dehydrated mixture is contacted with at least one dihaloaromatic compound under polymerization conditions.

#### DETAILED DESCRIPTION OF THE INVENTION

The poly(arnlene sulfide) polymer is prepared according to this invention by pre-reacting reactants comprising an aqueous alkali metal hydroxide and a polar organic compound at a first temperature to form a mixture, then reacting the mixture with a sulfur source at a second temperature under conditions sufficient to remove at least a portion of the water that is contained in the mixture, thereafter contacting the thus dehydrated mixture with at least one dihaloaromatic compound under polymerization conditions.

Any suitable sulfur source can be employed in the process of this invention. Suitable sulfur sources are disclosed in U.S. 3,919,177, which is hereby incorporated by reference. Such suitable sulfur sources include, but are not limited to thiosulfates, thioureas, thioamides, elemental sulfur, thiocarbamates, metal disulfides and oxysulfides, thiocarbonates, organic mercaptans, organic mercaptides, organic sulfides, alkali metal sulfides and bisulfides and hydrogen sulfide.

The alkali metal sulfide which can be employed in the production of poly(arnlene sulfide) polymers can be used as a hydrate or as an aqueous mixture. Alkali metal sulfides useful in this invention include lithium sulfide, sodium sulfide, potassium sulfide, rubidium sulfide, cesium sulfide, and mixtures thereof. The

- 3 -

aqueous solution of the alkali metal sulfide can be prepared according to this invention by the reaction of an alkali metal hydroxide with an alkali metal bisulfide in aqueous solution. It is generally preferred to use sodium sulfide or a combination of sodium bisulfide and sodium hydroxide as the sulfur source in the preparation of poly(arlene sulfide) polymers due to cost and effectiveness. In this invention which pre-reacts the alkali metal hydroxide and polar organic compound, it is preferred to use an alkali metal bisulfide as the sulfur source.

The polar organic compounds useful in the present invention are solvents for the dihaloaromatic compounds and the sulfur source used in the production of poly(arlene sulfide) polymers. Examples of such polar organic compounds include amides, including lactams, and sulfones. Specific examples of such polar organic compounds include hexamethylphosphoramide, tetramethylurea, N,N'-ethylenedipyrrolidone, N-methyl-2-pyrrolidone (NMP), pyrrolidone, caprolactam, N-ethylcaprolactam, sulfolane, N,N'-dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, low molecular weight polyamides, and the like. The polar organic compound presently preferred is NMP.

The hydrous or aqueous sulfur source and polar organic compound are pre-reacted (dehydrated) under conditions sufficient to remove at least a portion of the water prior to addition of the dihaloaromatic compound and commencement of the polymerization.

It has been found that the corrosiveness of the mixture to be dehydrated can advantageously and surprisingly be reduced by performing the pre-reaction in a two-step process. First, the aqueous alkali metal hydroxide is contacted with the polar organic compound at a first temperature, then the mixture is contacted with the alkali metal bisulfide at a second higher temperature and subjected to conditions sufficient to remove at least a portion, if not all, of the water prior to contacting the mixture with the remaining components of the reaction mixture. In another embodiment of the invention, the reaction product of the alkali metal hydroxide and polar organic compound is subjected to a higher temperature under conditions sufficient to remove a portion of the water prior to contacting the mixture with the alkali metal bisulfide.

The aqueous alkali metal hydroxide is contacted with the polar organic

- 4 -

compound for a time sufficient to allow reaction of the two components and the formation of an alkali metal aminoalkanoate in an aqueous solution. The reaction product of the alkali metal hydroxide and polar organic compound is far less corrosive and further has the advantage of being soluble in the polymerization reaction mixture.

- 5 In an especially preferred embodiment of this invention, sodium hydroxide and N-methyl-2-pyrrolidone are reacted to form N-methyl-4-aminobutanoate (SMAB).

The temperature at which the first step contacting takes place can vary widely, but it generally between about 50 and about 200°C. It is preferred to employ a temperature that is just above that necessary to cause the reactants to remain in  
10 solution since the corrosivity of the solution increases with increases in temperature. It is most preferred to employ a temperature in the range of about 75 to about 125°C.

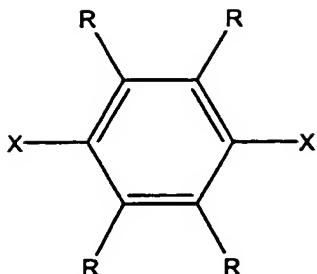
After the reaction of the alkali metal hydroxide and polar organic compound has taken place, the temperature is increased to a second temperature sufficient to effect dehydration of, or to further dehydrate, the mixture. If the alkali  
15 metal bisulfide that is to be employed is an aqueous sulfur source, it can be added prior to the dehydration and the dehydration can be effectively conducted to remove that water added with the sulfur source as well. Alternatively, separate dehydrations can be conducted after each addition of an aqueous reactant.

The dehydration can be conducted according to any method known to those of ordinary skill in the art. Suitable methods are disclosed in US 4,368,321 and U.S. 4,371,671, both of which are hereby incorporated by reference. The temperature at which the dehydration is conducted will generally range from about 100 to about 240°C; the pressure will typically range from slightly above atmospheric pressure up to 308 kPa (30 psig).

25 Generally, the remaining components of the reaction mixture can be contacted with each other in any order.

Dihaloaromatic compounds which can be employed in the process of this invention can be represented by the formula

- 5 -



where each X is selected from the group consisting of chlorine, bromine, and iodine, and each R is selected from the group consisting of hydrogen and hydrocarbyl in which the hydrocarbyl can be an alkyl, cycloalkyl, or aryl radical or combination thereof such as alkaryl, aralkyl, or the like, the total number of carbon atoms in each molecule being 5 within the range of 6 to about 24. While the halogen atoms can be in any position in the dihaloaromatic compound, it is preferred to employ p-dihalobenzenes as the dihaloaromatic compound.

Examples of suitable p-dihalobenzenes include p-dichlorobenzene (DCB), p-dibromobenzene, p-diiodobenzene, 1-chloro-4-bromobenzene, 1-chloro-4-10 iodobenzene, 1-bromo-4-iodobenzene, 2,5-dichlorotoluene, 2,5-dichloro-p-xylene, 1-ethyl-4-isopropyl-2,5-dibromobenzene, 1,2,4,5-tetramethyl-3,6-dichlorobenzene, 1-butyl-4-cyclohexyl-2,5-dibromo- benzene, 1-hexyl-3-dodecyl-2,5-dichlorobenzene, 1-octadecyl-2,5-diiodobenzene, 1-phenyl-2-chloro-5-bromobenzene, 1-(p-tolyl)-2,5-dibromobenzene, 1-benzyl-2,5-dichlorobenzene, 1-octyl-4-(3-methylcyclopentyl)-2,5-15 dichloro-benzene and the like, and mixtures of any two or more thereof. The preferred dihaloaromatic compound for use in this invention is p-dichlorobenzene (DCB) due to availability and effectiveness.

It is within the scope of this invention to employ other components in the polymerization reaction mixture or during the polymerization. For example, 20 molecular weight modifying or enhancing agents such as alkali metal carboxylates, lithium halides, or water can be added or produced during polymerization. Suitable alkali metal carboxylates which can be employed include those having the formula R'COOM where R' is a hydrocarbyl radical selected from alkyl, cycloalkyl, aryl, alkylaryl, arylalkyl, and the number of carbon atoms in R' is in the range of 1 to about 25 20, and M is an alkali metal selected from lithium, sodium, potassium, rubidium and

- 6 -

cesium. The alkali metal carboxylate can be employed as a hydrate or as a solution or dispersion in water. The preferred alkali metal carboxylate is sodium acetate due to availability and effectiveness.

Poly(arlene sulfide) polymerizations are generally disclosed in the art.

5 For example, U.S. 3,354,129, which is hereby incorporated by reference, U.S. 3,919,177, and U.S. 4,645,826 all disclose methods of preparing poly(arlene sulfide) polymers. The above-cited patent publications also disclose methods for recovering a useful poly(arlene sulfide) polymer product. Another suitable method of recovering poly(arlene sulfide) polymer products is disclosed in U.S. 4,415,729, which is hereby 10 incorporated by reference. These patent publications all describe the separation of a desired polymer product from reaction mixtures containing various impurities and unreacted polymerization components.

The poly(arlene sulfide) polymer prepared by the invention method can be either high or low molecular weight polymer. When describing the polymer 15 prepared by the invention method, the term low molecular weight poly(arlene sulfide) polymer is generally meant to denote a poly(arlene sulfide) polymer having a melt flow value in the range of greater than 1000 g/10 min. to about 30,000 g/10 min. when measured according to ASTM D 1238, Condition 316/5.

The term high molecular weight poly(arlene sulfide) polymer, as used 20 herein, is generally meant to denote an essentially linear poly(arlene sulfide) polymer having a melt flow value less than about 1000 g/10 min when in an uncured state. Essentially linear poly(arlene sulfide), as used herein, is defined as a polymer having no branching or such a small amount of branching as to have substantially no effect on the polymer properties. For example, the amount of polyhaloaromatic impurity found 25 in the dihaloaromatic used in the poly(arlene sulfide) polymerization process would not be sufficient to cause the resultant poly(arlene sulfide) to be outside the essentially linear definition).

Generally, the ratio of reactants employed in the polymerization process can vary widely. It is preferred that the molar ratio of the amount of dihaloaromatic 30 compound to amount of sulfur source be in the range of about 0.8/1 to about 2/1. If an alkali metal carboxylate is employed as a molecular weight modifying agent, it is

- 7 -

preferred that the molar ratio of alkali metal carboxylate to dihaloaromatic compound be within the range of about 0.05/1 to about 4/1.

5 The amount of polar organic compound employed can vary during the polymerization over a wide range. Preferably, however, during polymerization the molar ratio of the amount of polar organic compound to the amount of sulfur source is in the amount of 1/1 to 10/1.

The term commencement of the polymerization as used herein is defined as that point at which the polymerization reaction mixture is first subjected to polymerization conditions sufficient to initiate polymerization. The term termination 10 of polymerization, as used herein, is defined as that point at which an affirmative step is taken to effect a removal of the conditions necessary for polymerization to effectively continue, for example, by beginning the recovery of the poly(arlene sulfide) polymer from the polymerization mixture. It must be noted that use of the term termination of the polymerization does not imply that complete reaction of the 15 polymerization reaction components has occurred. It should also be noted that, as used herein, the term termination of the polymerization is not meant to imply that no further polymerization of the reactants can take place. Generally, for economic reasons, poly(arlene sulfide) polymer recovery is typically begun at a time when polymerization is substantially completed, that is, the increase in polymer molecular weight which 20 would result from further polymerization is not significant enough to warrant the additional polymerization time.

Although the reaction temperature at which the polymerization is conducted can vary over a wide range, generally it will be within the range of about 170°C (347°F) to about 325°C (617°F), preferably about 200°C to about 290°C. The 25 reaction time can vary widely, depending in part on the reaction temperature, but generally will be within the range of about 10 minutes to about 72 hours, preferably about 1 hour to about 8 hours. The pressure should be sufficient to maintain the polar organic compound and the dihaloaromatic compound substantially in the liquid phase.

The poly(arlene sulfide) polymer prepared according to this invention 30 can be recovered by any method known to those of ordinary skill in the art.

The following examples are provided in order to further illustrate the

invention, but are not intended to be limiting of the scope thereof.

#### EXAMPLES

In the following examples, the polymer extrusion rates, reported as grams per 10 minutes (g/10 min), were determined by the method of ASTM D 1238,

- 5 Condition 316/0.345. The orifice used for measuring the extrusion rate had a 2.096 +/- 0.005 mm diameter and a 31.75 +/- 0.05 mm length. Polymer melt flow values, in units of g/10 min, were determined by the method of ASTM D 1238, Condition 316/5. The orifice used for measuring the melt flow had a 2.096 +/- 0.005 mm diameter and a 8.000 +/- 0.025 mm length.

10 The relative amounts of volatiles present in the polymer samples were measured using a quartz crystal microbalance (QCM). This test involved vaporizing volatile materials from a molten PPS sample, collecting the vapors on a water cooled, vibrating quartz crystal, and ranking the amount of condensed material by changes in the frequency of the vibrating crystal. A weighed sample of the PPS polymer was  
15 placed in the bottom of a heated (325° C) stainless steel beaker that was covered with a lid containing the vibrating crystal. As the vapors condensed on the crystal, the resonance frequency of the crystal decreased in proportion to the amount deposited. Test values are reported in terms of a dimensionless relative number proportional to the change in frequency of the crystal in a 10 minute test time. Lower reported values  
20 indicate that the test sample had a lower level of volatiles at the test temperature than the samples with higher QCM values.

Analysis of polymers for unreacted dichlorobenzene in the crude reaction mixture was performed by gas chromatography (GC) of DCB/NMP mixtures using an HP 5890 gas chromatograph controlled by an HP 3365 Series II ChemStation  
25 (DOS Series). The carrier gas used was helium. Standard solutions were used to determine response factors. Injections of solutions to be analyzed were made using a 0.5 microliter syringe, typically using a 0.05-0.4 microliter injection. The column used with the gas chromatograph was a 30 meter 0.53 mm capillary column (DB Wax), purchased from J&W Scientific (Cat. No. 125-7032). The temperature program for  
30 DCB/NMP analysis first employed a hold at 120°C for 2 minutes, then temperature was ramped at 30°C/minute up to 190°C and held there for 1.30 minutes. Total

- 9 -

- analysis time was approximately 5.63 minutes. Typical mixtures ranged from about 0.1 weight percent *p*-dichlorobenzene in NMP up to about 4 weight percent *p*-dichlorobenzene in NMP. The GC standard used for comparison purposes was a mixture that was 1.5 weight percent *p*-dichlorobenzene in NMP and whose 5 compositions was known accurately. The standard solutions were diluted with isopropanol in order to fall within the desired concentration range. Experimental samples of a crude PPS reaction mixture from the reactor were blended with about a 10-fold amount of isopropanol in a Waring blender. Filtration of the sample yielded a clear liquid containing isopropanol, NMP and unreacted *p*-dichlorobenzene.
- 10           Metals analysis was performed by inductively coupled plasma/mass spectroscopy on aqueous nitric acid digests of the ash remaining from pyrolysis of samples of the polymers. The metals concentrations are reported in parts per million (ppm).

Example I

- 15           This example (Polymerization Run I-1) describes the general preparation of a poly(*p*-phenylene sulfide) polymer, (PPS), according to generally known methods. In this typical PPS preparation, to a one-liter stirred stainless steel reactor were added 40.97 grams sodium hydroxide (NaOH) pellets of 98.6 % purity (1.01 g-mol NaOH) and 40.0 g double distilled water (2.22 g-mol), 95.49 g aqueous 20 sodium bisulfide (NaSH) (58.707 % NaSH by weight) (1.00 g-mol), and 198.26 g of N-methyl-2-pyrrolidone (NMP) (2.00 g-mol). The reactor was degassed with 5 pressure release cycles of 446 kPa (50 psig) nitrogen and 5 cycles of 1479 kPa (200 psig) nitrogen. The reactor and contents were then heated slowly to 100°C, whereupon the dehydration outlet was opened and nitrogen flow at the rate of 32 25 mL/min. was begun. The dehydration was continued while heating to a final temperature of about 204°C. Then the dehydration outlet was closed and 148.49 g *p*-dichlorobenzene (DCB) (1.0 g-mol) dissolved in 1.00 g-mol NMP was charged to the reactor using a charge cylinder. The charge cylinder was rinsed with an additional 1 g-mol of NMP which was also added to the reactor. The reactor was degassed again in 30 the same manner as described above. The reactor was then heated to polymerization conditions (235°C) for 2 hours, then the temperature was increased to 260°C for 2 hrs

- 10 -

to produce PPS. At the conclusion of the polymerization, the reactor was cooled to room temperature and the mixture of PPS polymer and NMP was extracted using isopropanol.

The PPS in NMP/isopropanol was analyzed by gas chromatography to obtain a wt% DCB. The reactor product was then washed with water six times at 5 90°C and filtered on a coarse filter paper to recover the PPS product which was left to dry overnight under a hood. The following day, the PPS product was placed in a vacuum oven and dried at 100°C for 24 hours to yield 101.23 g of dried PPS polymer product. The extrusion rate of the PPS product was measured as described above and 10 found to be 72.71 g/10 min.

#### Example II

This example describes the effect of employing the invention method of pre-contacting the sodium hydroxide and NMP and dehydrating prior to adding the sodium bisulfide. For polymerization Run II-1, the reactor was charged with 40.97 15 grams sodium hydroxide (NaOH) pellets of 98.6 % purity (1.01 g-mol NaOH), 79.43 g double distilled water (4.41 g-mol) and 198.26 g of N-methyl-2-pyrrolidone (NMP) (2.00 g-mol). The reactor was degassed with 5 pressure release cycles of 446 kPa (50 psig) nitrogen and 5 cycles of 1479 kPa (200 psig) nitrogen. After the reactor had been degassed with nitrogen, the contents were heated to 100°C and held at that temperature 20 for a period of 1 hour. Thereafter, the dehydration outlet was opened and dehydration was carried out while increasing the temperature to about 204°C. Then, the dehydration outlet was closed and the reactor contents cooled to room temperature.

Following this first dehydration, 95.49 g aqueous sodium bisulfide (NaSH) (58.707 % NaSH by weight) (1.00 g-mol) was added to the reactor which was 25 degassed again as described above, except that 377 kPa (40 psig) of nitrogen was left in the reactor overnight. The next day the pressure was released and the reactor was heated to 105°C after which the dehydration outlet was opened. The reactor was further heated to about 204°C and then the outlet was closed. Thereafter, 1.01 g-mol of DCB (148.49 g) and 1.00 g-mol NMP were added to the dehydrated mixture and the 30 reactor was heated to 235°C and held for one hour. The reactor was then heated to 265°C and held for two hours. Then, the reactor was cooled and opened. A sample of

the liquid in the reactor was removed. The PPS product was mixed with isopropanol, then filtered and washed with distilled water 6 times at a temperature of 90°C, then filtered to recover a polymer product. Approximately 102.08 g of PPS with an extrusion rate of 62.64 g/10 min was obtained after drying.

5 Run II-2 (38218-98) was carried out using the procedure described for Run II-1, except that the amount of water added in the first charge was approximately 2.22 g-mol instead of 4.41 g-mol and that 95.30 g of NaSH was added in the second charge to the reactor.

A comparison of the products from Example I and Example II, Runs 1  
10 and 2 is shown in Table I hereinbelow. The polymers produced by the invention method have comparable extrusion rates to that produced by known methods; however, the polymers produced by the invention method exhibit far lower levels of metals contamination, especially with respect to Chromium, Iron, and Nickel which are materials of construction of the reaction vessel. The lower levels of metals found  
15 in the final polymer product are an indication of less corrosivity in the reactor.

### Example III

Two additional PPS polymerization Runs III-1 and III-2 was carried out in the manner described in Example II, Run II-2 to further demonstrate the invention effect of pre-contacting the alkali metal hydroxide with the polar organic compound  
20 prior to adding the sulfur source.

Polymerization Run III-3 was performed in the manner set forth in Example I to provide an additional comparison employing known methods of polymerization.

The runs from this example are summarized in Table I. The use of the  
25 invention method of pre-contacting the alkali metal hydroxide with the polar organic compound at relatively lower temperatures, then adding the sulfur source and conducting a dehydration results in greatly decreased corrosiveness of the dehydration mixture, as evidenced by the much lower levels of metal contamination in the resultant polymer, compared with control Runs I-1 and III-3, with essentially the same extrusion  
30 rates.

- 12 -

Table I

Ex. Run No.	No. of dehy- dration Steps	Isopropanol extractables wt% DCB	Yield of PPS (g)	Extrusion Rate (g/10min.)	10 min. QCM	Na (ppm)	Cr (ppm)	Fe (ppm)	Ni (ppm)
5	I-1	1.1730	101.23	72.71	0.28	489	108	492	41.1
	II-1	2.070	102.08	62.64	0.278	443	6.8	39.3	8.9
	II-2	2.12150	100.75	35.61	0.275	367	14.5	55.2	9.1
	III-1	2.08930	101.46	37.54	0.351	379	11.2	45.6	14.5
	III-2	2.09905	101.45	48.5	0.345	409	11.1	37.2	9.3
	III-3	1.09520	100.48	56.04	0.328	375	132	558	52.4

While this invention has been described in detail for the purpose of illustration, it is not meant to be limited thereby, but is intended to cover all reasonable modifications within the scope thereof.

CLAIMS

1. A process for preparing a poly(arene sulfide) polymer which comprises:
  - (a) pre-reacting an aqueous alkali metal hydroxide with a polar organic compound at a first temperature to form a solution comprising an alkali metal aminoalkanoate;
  - (b) contacting the solution of step (a) with an alkali metal bisulfide and subjecting the thus formed mixture to a second temperature that is higher than said first temperature and that is sufficient to remove at least a portion of the water from such mixture; and
  - (c) then contacting the mixture with additional polymerization reactants comprising at least one dihaloaromatic compound under polymerization conditions.
2. A process according to claim 1, wherein said additional polymerization reactants also comprise a molecular weight modifying agent selected from the group consisting of alkali metal carboxylates, lithium halides, and water.
3. A process according to claim 2, wherein said molecular weight modifying agent is an alkali metal carboxylate.
4. A process according to claim 3, wherein said alkali metal carboxylate is sodium acetate.
5. A process according to claim 1, wherein the molar ratio of the amount of said dihaloaromatic compound to said sulfur source is in the range of about 0.8/1 to about 2/1.
6. A process according to claim 1, wherein the molar ratio of the amount of said polar organic compound to said sulfur source is in the range of about 1/1 to about 10/1.
7. A process according to claim 1, wherein said alkali metal hydroxide is sodium hydroxide.
8. A process according to claim 1, wherein said polar organic compound is N-methyl-2-pyrrolidone.
9. A process according to claim 1, wherein said alkali metal bisulfide is sodium bisulfide.
10. A process according to claim 1, wherein the molar ratio of said polar organic compound to the amount of said alkali metal bisulfide is in the range of about 1/1 to about 10/1.
11. A process according to claim 1, wherein said first temperature is in the range of about 50 to about 200°C.
12. A process according to claim 11, wherein the temperature is in the range of

75 to 125°C.

13. A process according to claim 1, wherein said second temperature is in the range of about 100 to about 240°C.

14. A process according to claim 1, wherein step (b) is conducted at a pressure in the range of atmospheric pressure to about 308 kPa (30 psig).

15. A poly(arlene sulfide) polymer prepared according to the process of claim 1.

16. A process for preparing a poly(arlene sulfide) polymer which comprises:

10 (a) pre-reacting an aqueous alkali metal hydroxide with a polar organic compound at a first temperature to form a solution comprising an alkali metal

aminoalkanoate;

15 (b) subjecting the aqueous solution to conditions of time and a second temperature which is higher than said first temperature and that is sufficient to remove substantially the water in such solution;

(c) contacting the solution from step (b) from which water has been

15 substantially removed with an aqueous alkali metal bisulfide and subjecting the thus formed mixture to conditions of time and temperature sufficient to remove substantially the water in such solution; and

20 (d) then contacting the mixture with additional polymerization reactants comprising at least one dihaloaromatic compound under polymerization conditions.

20 17. A process according to claim 16, wherein said additional polymerization reactants also comprise a molecular weight modifying agent selected from the group consisting of alkali metal carboxylates, lithium halides, and water.

18. A process according to claim 17, wherein said molecular weight modifying agent is an alkali metal carboxylate.

25 19. A process according to claim 18, wherein said alkali metal carboxylate is sodium acetate.

20. A process according to claim 16, wherein the molar ratio of the amount of said dihaloaromatic compound to said sulfur source is in the range of about 0.8/1 to about 2/1.

21. A process according to claim 16, wherein the molar ratio of the amount of 30 said polar organic compound to said sulfur source is in the range of about 1/1 to about 10/1.

22. A process according to claim 16, wherein said alkali metal hydroxide is sodium hydroxide.

23. A process according to claim 16, wherein said polar organic compound is N-methyl-2-pyrrolidone.

- 15 -

24. A process according to claim 16, wherein said alkali metal bisulfide is sodium bisulfide.
25. A process according to claim 16, wherein the molar ratio of said polar organic compounds to the amount of said alkali metal bisulfide is in the range of about 1/1 to about 5 10/1.
26. A process according to claim 16, wherein said first temperature is in the range of about 50 to about 240°C.
27. A process according to claim 27, wherein the temperature is in the range of 75 to 125°C.
- 10 28. A process according to claim 16, wherein said second temperature is in the range of about 100 to about 240°C.
29. A process according to claim 16, wherein steps (b) and (c) are conducted at a pressure independently selected from the range of atmospheric pressure to about 307 kPa (30 psig).
- 15 30. A poly(arlene sulfide) polymer produced according to the process of claim 16.